



Effect of primer on honeycomb-supported $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_{3\pm\delta}$ perovskite for methane catalytic flameless combustion

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Received 11 November 2002; received in revised form 15 January 2003; accepted 19 January 2003

Abstract

A set of $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_3$ combustion catalysts, supported onto commercial cordierite monoliths, through either La_2O_3 or Al_2O_3 as primer, was prepared with different active phase/primer combinations. Two different salts were tested as precursors of the La-based primer. The behaviour of the catalysts for the methane flameless combustion was compared with that of samples prepared in the absence of any primer. The primers and the active phase were deposited by means of the dip-coating technique. The preparation conditions of the suspension and/or solution for the dip coating were studied, aiming at obtaining a uniform and resistant deposition. The catalysts were characterised, before and after the activity tests, by BET, X-ray diffraction analysis (XRD) and scanning electron microscope (SEM). The comparison between the catalysts showed that with Al_2O_3 as primer the catalyst possesses a higher surface area (SA) and hence a higher initial activity, while with La_2O_3 as primer a very high thermal stability can be obtained.

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Keywords: Perovskite catalyst; La_2O_3 and Al_2O_3 as primer; Honeycomb support; Dip coating; Methane catalytic flameless combustion

1. Introduction

Chemical processes based on heterogeneous catalysis represent one of the principal means to reduce environment pollution. In the last few years, the production of catalysts with monolithic structure has increased steadily. In particular, catalysts with honeycomb structure are used in abators of gaseous pollutants in nitric acid factories and in thermo-electrical power stations and can be used in catalytic combustors to suppress the formation of the gaseous pollutants (such as NO_x and CO) forming in the usual high temperature hydrocarbon combustion [1]. Furthermore, the catalytic mufflers based on the three way catalyst (TWC) can

remove over 90% of the emission of CO, hydrocarbons and NO_x . The TWC consists of a thin layer of active phase deposited by dip coating on a multi-channel, honeycomb-shaped ceramic material, usually made of cordierite. Seventy to eighty percent of the coating consists of high surface area (SA) $\gamma\text{-Al}_2\text{O}_3$, 10–20% is an oxide mixture (e.g. Ba-Ni-Zr-Ce-O) and 10% is the active phase (Rh, Pt and Pd). The function of the oxide fraction, especially of cerium oxide, is that of a buffer, storing and releasing the oxygen needed by the reaction [2]. Moreover, cerium oxide can stabilise the dispersion of the active phase [3].

The use of structured catalysts for an increasing number of reactions is due to the substantial reduction of reactants pressure drop across the catalyst bed, ensured by these catalysts. In order to favour the adhesion of the active phase to the monolith support, the

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pre-coating of the honeycomb with a primer is needed. This usually brings about also an increase of surface area and improves the stability of the catalyst [4]. The most commonly used primer is γ - Al_2O_3 , which however shows a relatively poor stability at high temperature, leading to a more or less rapid catalyst decay. In order to improve heat resistance, many studies are presently carried out on doped alumina or on different mixed oxides (e.g. Zr-Ce-Ti-Mg-O) [5,6].

Furthermore, perovskite-like structured mixed oxides, and especially $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_{3\pm\delta}$ [1], proved since long time a valuable alternative to noble metals as active phase for total oxidation of hydrocarbons, being much cheaper, thermally stable and comparatively active [7].

The aim of the present work was then the preparation of a series of honeycomb-supported $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_{3\pm\delta}$ catalysts for the low-temperature catalytic flameless combustion (CFC) of methane. Two primers were compared, Al_2O_3 and La_2O_3 , the latter prepared from two different precursors, by analysing their physical and mechanical properties, together with their influence on both catalytic activity and on thermal deactivation rate. La_2O_3 , in spite of its relatively low surface area, was chosen as an innovative possible substitute for alumina, because it contains only elements present in the active phase, so avoiding the addition of undesired dopants, and because it is known to be thermally more stable [8]. Finally, the effect of different loadings of primer and/or of active phase on catalyst activity and stability was investigated.

2. Experimental

2.1. Active phase preparation

The active phase, $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_{3\pm\delta}$, was prepared through two different routes: the so called sol–gel citrates (SGC) method [9] and the flame hydrolysis (FH) technique. A detailed description of the apparatus and of the conditions adopted for perovskites preparation through the FH method can be found elsewhere [10–12].

The SGC sample was prepared by dissolving $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich, purity $\geq 99.99\%$), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (ACROS, purity $\geq 99.50\%$) and $\text{Co}(\text{NO}_3)_2$ (Merck, purity $\geq 99.99\%$) in distilled water. Citric

acid (Aldrich, purity $\geq 99.0\%$) was added as complexing agent. The solvent was evaporated under vacuum at 70°C , until a very viscous gel was formed. Finally the latter was dried at 70°C and 90 mbar residual pressure and then calcined at 750°C in air.

The FH sample was prepared from a 2–3 wt.% aqueous solution of the same reactants. Citric acid was then added both as complexing agent and to increase the flame temperature [10] and the solution was nebulised on a $\text{H}_2 + \text{O}_2$ flame. The very thin powder formed was collected by means of an electrostatic precipitator.

2.2. Characterisation of fresh and aged catalysts

X-ray diffraction analysis (XRD) was done by means of a Philips PW 1820 diffractometer, using the Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418\text{ nm}$). Phase recognition was obtained by comparison with literature data [13].

BET surface area and porosity were measured by means of a Micromeritics ASAP 2010 instrument. To measure the BET SA of monoliths, a particular home-made test tube was needed, to host the sample. The results of BET analysis during the different steps of the preparation, before and after the reaction and after the life tests, are collected in Table 1.

A Cambridge Stereoscan 150 scanning electron microscope (SEM) was employed for the morphological analysis of the monolithic catalysts and for determining the particle size of the as-prepared perovskite powder. Several SEM micro-graphs have been collected, to investigate the dispersion and adhesion of the perovskite and of the primer on the cordierite surface.

2.3. Preparation of the primer suspension/solution

For the wash coating deposition of the primer a suspension or a solution of the component to be deposited is needed. To obtain a stable suspension, a tumbling ball milling procedure was employed, using a 50 ml cylindrical polypropylene jar containing six zirconia balls (10 mm in diameter). The alumina primer was obtained from commercial boehmite (Disperal P2 by Condea Chemie). The suspension was prepared by ball milling for 2 h, 2.5 g of boehmite in 22.5 ml of an aqueous solution of nitric acid (0.4 vol.%).

Table 1
BET surface area (m²/g)

Sample ^a	Perovskite powder	After primer loading	After perovskite loading	After activity test	After accelerated ageing test
H2 ^b	34.1	11.5	11.2	9.9	7.3
H9 ^c	34.1	1.7	2	1.7	1.0
H14 ^d	34.1	1.4	1.4	1.0	1.0
H18 ^{d,e}	18.6	1.4	1.5	1.1	1.1

^a Bare honeycomb BET surface area 0.3 m²/g.

^b Primer Al₂O₃.

^c Primer La₂O₃ from La acetate.

^d Primer La₂O₃ from La nitrate.

^e Active phase by FH method.

The precursors used to obtain the La₂O₃ primer were either La(NO₃)₃ or La(CH₃COO)₃·*n*H₂O. The first one is soluble in water, so neither the presence of HNO₃ as peptising agent, nor the ball milling procedure was needed. Different concentrations of the starting solution were used, according to the desired loading. By contrast, lanthanum acetate, poorly soluble in water, was ball milled for 2 h (1.5 g of salt in 22.5 ml of distilled water), so obtaining a suspension stable for weeks.

2.4. Preparation of the active phase suspension

To obtain a stable suspension, 0.8 g of perovskite powder, prepared either by the SGC method or by FH, were dispersed in ca. 20 cm³ of distilled water and ball milled for 4 h as described.

2.5. Dip coating

The monolith, in form of 1 cm diameter × 5 cm long cylinders, cut from commercial 60 channels/cm² cordierite honeycomb, was pre-dried at 500 °C for 1 h and weighed. The dip-coating technique consists in dipping and withdrawing at constant speed the honeycomb from the solution/suspension containing the desired component. The monolith was then suspended to a thin nylon line and kept with the channels direction normal to the surface of the suspension during the whole dipping and withdrawing operation. This was accomplished by means of a home-made apparatus [1], driven by a step by step motor through an interchangeable-gears gearbox.

Every dipping was followed by drying at room temperature for 10 min and calcination at 500 °C in air for 1.5 h. The dip coating, drying and calcination procedure was repeated several times, until the desired loading of primer and/or active phase was obtained. An example of uniformly coated finished catalyst is shown in Fig. 1, in comparison with a bare honeycomb support.

The loading was expressed as weight percent of the finished catalyst. The composition of all the catalysts prepared is listed in Table 2, where the samples can be divided in subsets, according to the nature of primer, to the active phase preparation method, to the primers' precursor, etc.

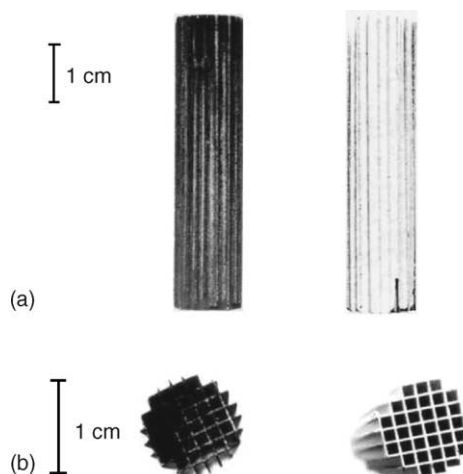


Fig. 1. Example of finished catalyst and of the bare honeycomb: (a) longitudinal view; (b) cross-view. Size of the square channels ca. 1.2 mm × 1.2 mm.

Table 2
The composition of prepared catalyst

Sample	Primer (wt.%)	Active phase (wt.%)
H1 ^a	5	1.8
H2 ^a	5	2
H3 ^a	5	3.5
H4 ^a	5	6
H5 ^a	2	3
H6 ^a	8	3
H7	–	6
H8	–	6 ^c
H9 ^b	2	2
H10 ^b	5	2
H11 ^b	8	2
H12 ^d	2	2
H13 ^d	3.5	2
H14 ^d	3.9	2
H15 ^d	7	2
H16 ^d	3.9	1
H17 ^d	3.9	4
H18 ^d	3.9	2 ^c

^a Primer Al₂O₃.

^b Primer La₂O₃ from lanthanum acetate.

^c Active phase from FH method.

^d Primer La₂O₃ from lanthanum nitrate.

2.6. Catalytic activity tests

The activity tests for the CFC of methane were carried out by means of a bench-scale continuous reactor. A detailed description of the reactor, of the procedure and of the apparatus for the gas analysis can be found elsewhere [1,11,12]. Briefly, an Incoloy 800 tubular reactor, 400 mm in length, inside diameter 10.5 mm and external diameter 15.7 mm, was put within two heavy metal blocks into a tubular furnace. The honeycomb was positioned in the isothermal middle part of the reactor between two flocks of quartz wool. The void part of the reactor tube, above and below the catalyst, was filled with quartz beads (10–20 mesh). The error of the GC analysis employed was $\pm 2\%$.

Prior to each run, the catalyst was activated in flowing air (20 cm³/min), while increasing temperature by 10 °C/min up to 600 °C, then kept for 1 h. The activity tests were carried out by feeding a mixture composed of 0.5 vol.% CH₄, 49.5 vol.% He and 50 vol.% air, while increasing temperature by 2 °C/min from 250 to 600 °C.

The total flux of the mixture was calculated by referring to the mass of active phase, so to have

for every test an identical value of time factor $\tau = W/F = 2.5$ mg of perovskite min/cm³ of gas overall flow rate. Hence, the overall flow rate ranged from 7 to 13 cm³/min.

2.7. Thermal deactivation accelerated tests

Some significant samples have been tested under particular conditions, to investigate their heat resistance. These tests were carried as follows by means of the same apparatus used for activity tests. At the end of the standard test an isotherm followed at the temperature (T_f) of maximum conversion, for 24 h. Then, some cycles of reaction/deactivation were accomplished, by increasing temperature (10 °C/min) up to 800 °C, then kept for 1 h. The temperature was then brought back to an isotherm at T_f , kept for 3 h, during which the catalytic activity was measured. The deactivation cycle was then repeated, till a decrease in conversion at T_f was noticed. The results are shown in Table 3.

3. Results and discussion

3.1. Characterisation of fresh active phase

The XRD pattern, relative to the powder prepared by the FH technique, showed the presence of the perovskite phase only (Fig. 2), while the sample prepared by the SGC method proved much less crystalline and showed the presence of traces of some phases other than the perovskite-like one. The better phase purity of the FH sample is due to the very high temperature (ca. 1600 °C) attained during the preparation, as extensively described elsewhere [10].

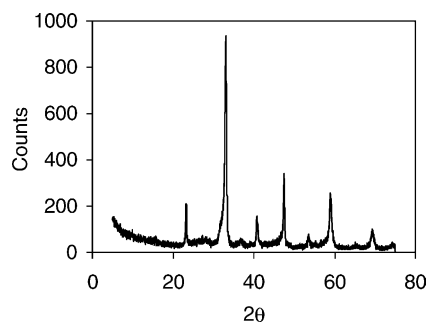


Fig. 2. XRD pattern of La_{0.9}Ce_{0.1}CoO_{3±δ} perovskite prepared by the FH method.

Table 3
Activity data before and after accelerated thermal deactivation tests

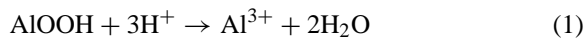
Sample	$T_{1/2}$	T_f	Conversion of CH ₄ at T_f (%)	Conversion of CH ₄ after 24 h at T_f (%)	Conversion of CH ₄ after 100 h at T_f (%)	Conversion of CH ₄ after first cycle (%)	Conversion of CH ₄ after second cycle (%)	Conversion of CH ₄ after third cycle (%)
H2	488	582	100	88.0	–	71.0	–	–
H7	490	604	100	100	100	89.2	86.0	83.0
H8	468	595	100	100	100	90.4	87.5	85.0
H9	452	570	97.3	96.1	–	82.0	81.5	–
H14	450	585	98.4	99.0	–	94.6	93.5	93.0
H18	459	580	98.0	98.0	–	99.0	95.0	95.0

BET SA of the catalysts obtained by FH was around 20 m²/g (Table 1). This is due to the very short residence time within the flame, that limits any deep sintering of the powder. The SGC sample showed an about double value of SA, being calcined at 750 °C only, which however affected considerably heat resistance [10].

For the FH-made catalyst SEM analysis showed clusters, 200–500 nm in size, made of highly uniform, nearly spherical particles, 20–80 nm in size [1].

3.2. pH effects on preparation of solution and/or suspension of primer

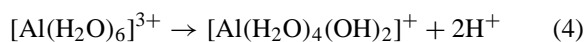
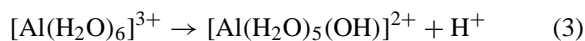
For the preparation of the alumina precursors' suspension, the presence of nitric acid showed very important, in order to improve the stability of the suspension and govern the thickness of the deposited layer [14]. Indeed, it is well-known [15] that a low pH of the solution favours the peptisation of the oxide



while at higher pH H⁺ ions interact with the surface of the solid precursor, leading to the establishment of an equilibrium between the solid and the solution



Moreover, Al³⁺ ions in aqueous solution form a water complex through the two equilibria [16]



Reactions (3) and (4), always present, contrast the increasing of pH through the dissolution of a part of the

boehmite and the protonation of the surface of solid particles. To minimise these phenomena and obtain a stable suspension, the optimal molar ratio between H⁺ and Al³⁺ lies around 0.05 [16].

A similar situation occurs during the preparation of the suspension of lanthanum oxide precursor. Indeed, at pH values ≥ 6.5 the precipitation of lanthanum hydroxide prevents the formation of a stable suspension and leads to a poorly uniform coating. On the other hand, at too low pH the La precursor cannot be easily adsorbed on the cordierite acidic surface. Then, we found that the optimal pH of the solution/suspension of La³⁺ should be around a value of 6.

3.3. Effect of the honeycomb withdrawing speed and of dipping time

One of the most important parameters to be controlled, in order to obtain a strong and uniform grafting of both primer and perovskite on the cordierite, is the speed of the honeycomb withdrawing during the dip coating. The optimal extraction speed depends on the rheological behaviour of the suspension of the material to be deposited. A high speed usually leads to an excessive and uneven deposition. In fact, the fluid in excess tends to accumulate at the bottom of the sample. By contrast, a too low speed involves a too thin liquid layer adhering to the solid surface, forcing to repeat several times the treatment in order to get the desired loading. Our preliminary experiments showed that, for the present suspensions (or solution) and support shape, the optimum speed for drawing out the honeycomb was ca. 10 cm/min.

Furthermore, with the present materials, the loading of La₂O₃ proved almost independent of dipping time, the equilibrium loading being attained quite rapidly.

Hence, for a uniform coating, the loading depended almost exclusively on the concentration of the solution/suspension.

3.4. Catalytic activity tests

The CFC of methane has been chosen as model reaction, because methane is very widely employed as fuel and it is the less reactive hydrocarbon. All the present catalysts proved highly active, leading to methane full conversion to carbon dioxide at $T \leq 650^\circ\text{C}$, under the selected reaction conditions (Fig. 3).

Fig. 3A shows the comparison between the catalysts with alumina as primer, with different loadings of primer and of active phase (catalysts H1–H6, Table 2). The most active catalysts showed H2 and H4, characterised by 5% loading of alumina and 2 and 6% loading of perovskite, respectively. Indeed, the sample H2 showed the most active at low temperature (i.e. below 400°C), while H4 showed the lowest

value of $T_{1/2}$ (ca. 455°C) within the present group, $T_{1/2}$ being the temperature at which the conversion of methane attained 50%. The temperature (T_f) of complete conversion was about the same (ca. 585°C) for both the catalysts. However, it can be noticed that perovskite loading does not affect catalytic performance to the same extent as primer loading, good results being attained even with active phase loading as low as 2 wt.%. Furthermore, it can be noticed from the same Fig. 3A, that by increasing Al_2O_3 content from 2 to 5 wt.% (samples H5 and H3, respectively) a considerable activity increase has been obtained, $T_{1/2}$ decreasing from 502 to 490°C and T_f decreasing from 630 to 590°C . A further increase of primer loading did not further improve catalytic performance appreciably. Indeed, on going from 5 wt.% (sample H3) to 8 wt.% (sample H6) loading of Al_2O_3 , only a slight decrease of $T_{1/2}$ was observed, T_f remaining 590°C for both samples. Hence, 5 wt.% primer loading was chosen as an optimal value from the point of view of activity.

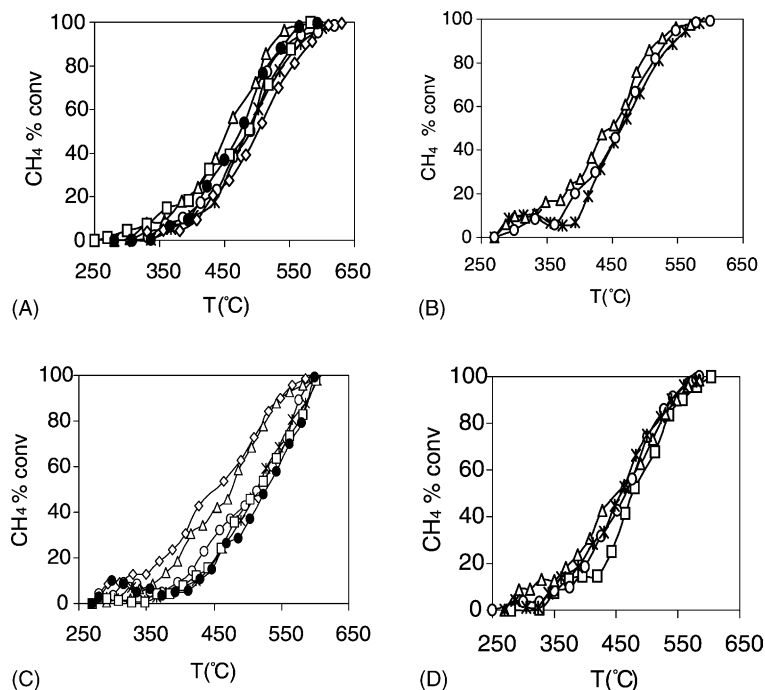


Fig. 3. Comparison between the catalysts: (A) with alumina as primer: (✱) H1, (□) H2, (○) H3, (△) H4, (◇) H5, (●) H6 (Table 1); (B) with different loading of lanthanum oxide from acetate and constant loading of perovskite (2%): (△) H9, (○) H10, (✱) H11; (C) with lanthanum oxide from nitrate: (✱) H12, (△) H13, (◇) H14, (○) H15, (□) H16, (●) H17; (D) with differently prepared perovskite and with or without primer: (□) H7, (○) H8, (△) H14, (✱) H18.

Fig. 3B shows the comparison between the catalysts with La_2O_3 from La-acetate as primer, (catalysts H9–H11, Table 2). The most active sample was H9 (2% primer and 2% perovskite). La_2O_3 showed immediately to be a very active primer also in so low amount (compare e.g. with sample H5, with 2 wt.% alumina). By comparing samples H2 and H9, characterised by the same perovskite loading (Table 2), one can see the higher performance of La-oxide as primer, with respect to alumina.

This seems not directly correlated to the surface area of the samples. Indeed, from Table 1 one may notice that the Al_2O_3 -based samples possess a much higher SA than the La_2O_3 -based ones. The reason of the lower activity of the Al_2O_3 -based catalysts likely should be due to the interaction between the components of the perovskite and the alumina primer. Indeed, it is well-known [17–19] that, at relatively low temperature (ca. 500 °C), the formation of a spinel structure such as CoAl_2O_4 can take place rather easily. The formation of this species transforms a part of the perovskitic ABO_3 active phase into the relatively inert spinel phase and it is mainly affected by two parameters, namely the temperature and the presence of water. Methane combustion supplies a sufficient amount of water to favour the partial migration of Co towards alumina, to form CoAl_2O_4 . Moreover, in other studies [20,21], carried out on $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ loaded on cordieritic honeycomb, the same reaction was observed at higher temperature (ca. 800 °C) even in dry atmosphere, leading to the catalytically less active CoAl_2O_4 . This phenomenon was not observed with perovskites of different B metal, such as Mn or Fe. However, La segregation from a LaCoO_3 perovskite to alumina was also reported, to form LaAlO_3 [22], accompanied by partial destruction of the perovskitic structure.

Fig. 3C (samples H12–H18, with La_2O_3 from nitrate) shows that the highest conversion was given by H14, characterised by a primer loading of ca. 4 wt.% and perovskite loading of 2 wt.% (Table 2). Hence, in order to obtain the same conversion of sample H9, the primer loading has to be doubled when passing from acetate to nitrate as precursor. Since the SA of the fresh samples H9 and H14 (Table 1) are very similar, we can infer that a double loading of primer is needed in order to obtain the same dispersion of perovskite. This is clearly due to the nature of the

primers' precursor. As a conclusion, based on catalytic activity only, all these data clearly show the advantage of La_2O_3 as primer, in spite of its lower surface area, especially when La_2O_3 is obtained from the acetate.

In addition, by varying the loading of the active phase at constant loading of primer (samples H14, H16, H17 Table 2) we observed a significant change of activity (Fig. 3C), at difference with what observed with alumina as primer. Indeed, due to the very low SA in the case of La_2O_3 as primer (compare e.g. H14 with H2, Table 1), an increase of active phase loading from 2 to 4 wt.% leads to a poor dispersion, penalising catalytic activity. This effect was not relevant with Al_2O_3 -primer based catalysts, due to the much higher SA after the addition of the primer, allowing to offer a high dispersion even with higher loading of the active phase. However, as expected, a too low perovskite loading (sample H16, 1 wt.%) showed insufficient.

Finally, Fig. 3D shows the activity of two catalysts without primer, both loaded with 6% perovskite (H7 and H8, Table 2), but obtained by the SGC and FH technique, respectively. They were compared with samples H14 and H18, characterised by 3.9% loading of lanthanum oxide (from nitrate) and 2% loading of perovskite, prepared through SGC and FH, respectively. The activity of samples H7 (SGC method) and H8 (FH method) is in line with what observed in our previous work [1]. Indeed, the present catalysts showed $T_{1/2}$ values of 475 and 460 °C and T_f values of 604 and 585 °C, respectively, confirming the better performance of the FH perovskite. The activity of the samples H8 and H18, both prepared from the same FH perovskite, was the same, showing that the FH active phase is substantially unaffected by the presence of the primer. By contrast, a considerable increase of activity was noticed, especially at low temperature, for sample H14, prepared from the SGC perovskite and supported on a primer-coated honeycomb. In this case an activity comparable to that of the FH samples was obtained. The low activity of sample H7 should then be connected to a different cause, namely to its thermal and mechanical instability (vide infra). Indeed, after the activity test the adhesion of the active phase to the support showed very poor for the H7 sample, so that a considerable portion of powdered active phase was found at the bottom of the honeycomb.

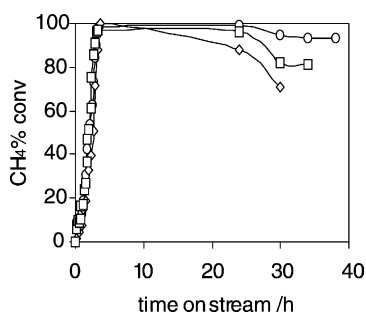


Fig. 4. Thermal stability tests for the catalysts with different primers: (○), H14 ($T_f = 585\text{ }^{\circ}\text{C}$); (◇), H2 ($T_f = 582\text{ }^{\circ}\text{C}$); (□), H9 ($T_f = 570\text{ }^{\circ}\text{C}$).

3.5. Thermal stability accelerated tests

The results of the thermal stability tests are collected in Table 3 and Fig. 4. The less stable catalyst was H2 (alumina as primer), which showed a progressively decreasing methane conversion from the initial 100 to 88% (after 24 h on-stream at $T_f = 582\text{ }^{\circ}\text{C}$) to 71% only (after the first accelerated ageing cycle). In addition to the possible formation of LaAlO_3 or CoAl_2O_4 phases, a further problem is connected to the poor thermal stability of alumina, leading to sintering, which strongly reduces the catalyst surface area. Furthermore, the different thermal dilation coefficient with respect to the cordieritic support can very likely be the cause of formation of the deep creeps observed in the coating (see Fig. 5). Indeed, fresh H2 sample showed

the highest surface area (ca. $12\text{ m}^2/\text{g}$), which strongly decreased (by ca. 20%) even after 100 h on-stream at T_f only and further dropped (by ca. 40%) after the first accelerated ageing test. Moreover, Fig. 5, besides the previously mentioned deep creeps, shows that the active phase adheres much better to the alumina primer than the latter to the cordierite. This confirms the possible formation of the mentioned La-aluminate and Co-aluminate as reaction products of the migration of La and Co into alumina and the poor adhesion of the latter to the cordierite, as a consequence of the different thermal dilation coefficient of the two materials. Thus, from all these considerations, alumina confirmed clearly unsuitable as primer to favour adhesion of our perovskitic catalyst to the honeycomb support.

The much better thermal stability of lanthanum oxide with respect to alumina is confirmed by sample H9 (Fig. 4 and Table 3) prepared from lanthanum acetate. However, this primer appeared still insufficient to guarantee an optimal thermal stability. Indeed, H9 sample showed 97.3% methane conversion, which decreased to 96% after 24 h on-stream at T_f and to ca. 82% after two ageing cycles (Table 3 and Fig. 4). This has been confirmed by SEM analysis (see Fig. 6), showing that both primer and active phase, though better grafted to the cordierite, tended to migrate onto the support surface and to accumulate in thicker layers at the crossing of the honeycomb walls, so leading to a considerable decrease of active phase surface area and hence of activity.

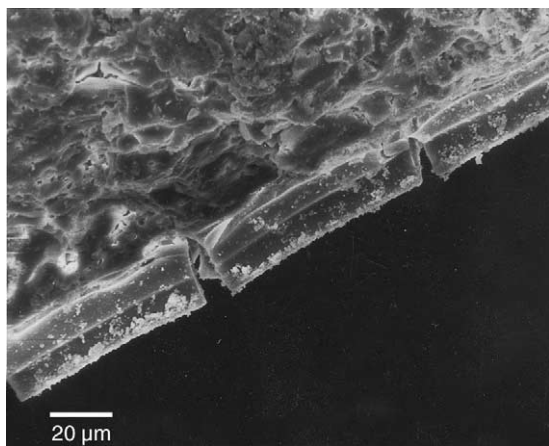


Fig. 5. Typical SEM image of a cross-section of H2 sample (primer alumina) after accelerated ageing.

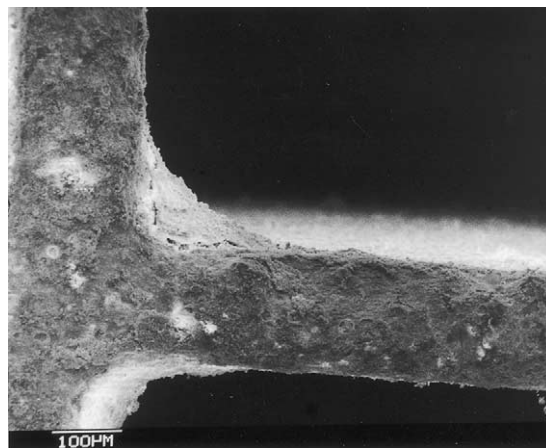


Fig. 6. Typical SEM image of a cross-section of H9 sample (primer La_2O_3 from acetate) after accelerated ageing.

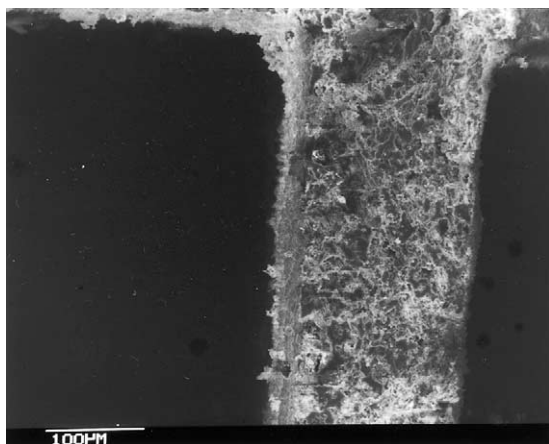


Fig. 7. Typical SEM image of a cross-section of H14 sample (primer La_2O_3 from nitrate) after accelerated ageing.

By contrast, H14 sample, prepared from lanthanum nitrate, showed about 99% methane conversion after 24 h on-stream at T_f and still 93% conversion after three ageing cycles (Fig. 4 and Table 3). Fig. 7 shows that this good performance is clearly connected with the much better grafting of primer and of active phase to the support and to a very uniform distribution of the materials onto the surface of the honeycomb, allowing a very good thermal stability of the catalyst even after three fast deactivation cycles. So one may conclude that the deposition of lanthanum oxide from $\text{La}(\text{NO}_3)_3$ gives the best results from the point of view of both activity (vide supra) and thermal stability.

The final set of tests aimed at comparing samples prepared in the presence or in the absence of primer. The data (Table 3) show that catalyst H8 (FH perovskite without primer, Table 2) was sufficiently stable during the first 24 h test and even after 100 h at T_f . However, the comparison of catalysts H8 and H18 (FH perovskite and La_2O_3 from nitrate as primer) confirmed the need of a thermally stable primer, to graft the perovskite to the honeycomb surface. Indeed, activity of H8 dropped to 85% after three accelerated ageing cycles. By contrast, the H18 sample maintained an acceptable activity during the whole durability test.

At last, the direct deposition of the SGC perovskite on the cordierite support (H7 sample) led to the worst results, due to the poor thermal stability of the catalyst

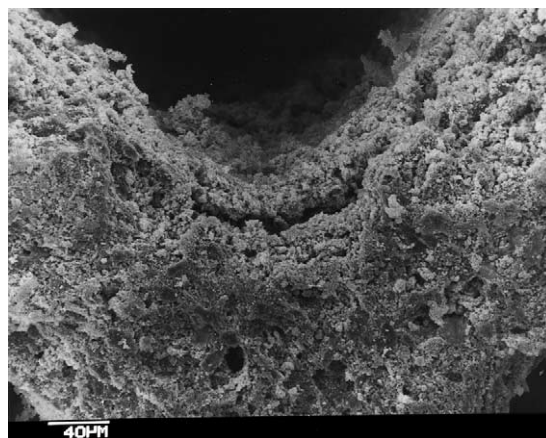


Fig. 8. Typical SEM image of a cross-section of H7 sample (without primer) after accelerated ageing.

itself, combined with the lack of a grafting agent. Indeed, SEM photos (Fig. 8) show the presence of deep cracks between the active phase and the cordierite surface. This led to the mentioned loosening of catalyst powder, found on the quartz wool at the bottom of the honeycomb.

4. Conclusions

- (i) In spite of its low surface area, La_2O_3 proved to be a very good primer, in comparison with alumina, for grafting the $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_{3\pm\delta}$ catalyst onto cordieritic honeycomb support, from the points of view of both activity and thermal stability, especially when prepared from the nitrate as precursor.
- (ii) The most critical parameters for attaining a good dispersion of both the primer and the catalyst on the support and a strong grafting to the latter are the honeycomb withdrawing speed and the concentration of the suspension/solution of the material to be deposited, which affects the rheology of the solution/suspension. Immersion time seems not to play a substantial role.

Acknowledgements

The financial aid of the Italian Council for Research (CNR), through the PF-MSTA-II, is gratefully acknowledged.

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